

H = Hourly heat input in mmBtu, as calculated using the procedures in section 5 of appendix F of this part.

Uf=1/385 scf CO<sub>2</sub>/lb-mole at 14.7 psia and 68 °F.

### 3. PROCEDURES FOR ESTIMATING CO<sub>2</sub> EMISSIONS FROM SORBENT

When the affected unit has a wet flue gas desulfurization system, is a fluidized bed boiler, or uses other emission controls with sorbent injection, use either a CO<sub>2</sub> continuous emission monitoring system or an O<sub>2</sub> monitor and a flow monitor, or use the procedures, methods, and equations in sections 3.1 through 3.2 of this appendix to determine daily CO<sub>2</sub> mass emissions from the sorbent (in tons).

3.1 When limestone is the sorbent material, use the equations and procedures in either section 3.1.1 or 3.1.2 of this appendix.

3.1.1 Use the following equation to estimate daily CO<sub>2</sub> mass emissions from sorbent (in tons).

$$SE_{CO_2} = W_{CaCO_3} F_u \frac{MW_{CO_2}}{MW_{CaCO_3}}$$

(Eq. G-5)

where,

SE<sub>CO<sub>2</sub></sub>=CO<sub>2</sub> emitted from sorbent, tons/day.

W<sub>CaCO<sub>3</sub></sub>=CaCO<sub>3</sub> used, tons/day.

F<sub>u</sub>=1.00, the calcium to sulfur stoichiometric ratio.

MW<sub>CO<sub>2</sub></sub>=Molecular weight of carbon dioxide (44).

MW<sub>CaCO<sub>3</sub></sub>=Molecular weight of calcium carbonate (100).

3.1.2 In lieu of using Equation G-5, any owner or operator who operates and maintains a certified SO<sub>2</sub>-diluent continuous emission monitoring system (consisting of an SO<sub>2</sub> pollutant concentration monitor and an O<sub>2</sub> or CO<sub>2</sub> diluent gas monitor), for measuring and recording SO<sub>2</sub> emission rate (in lb/mmBtu) at the outlet to the emission controls and who uses the applicable procedures, methods, and equations in §75.15 of this part to estimate the SO<sub>2</sub> emissions removal efficiency of the emission controls, may use the following equations to estimate daily CO<sub>2</sub> mass emissions from sorbent (in tons).

$$SE_{CO_2} = F_u \frac{W_{SO_2}}{2000} \frac{MW_{CO_2}}{MW_{SO_2}}$$

(Eq. G-6)

where,

SE<sub>CO<sub>2</sub></sub>=CO<sub>2</sub> emitted from sorbent, tons/day.

MW<sub>CO<sub>2</sub></sub>=Molecular weight of carbon dioxide (44).

MW<sub>SO<sub>2</sub></sub>=Molecular weight of sulfur dioxide (64).

W<sub>SO<sub>2</sub></sub>=Sulfur dioxide removed, lb/day, as calculated below using Eq. G-7.

F<sub>u</sub>=1.0, the calcium to sulfur stoichiometric ratio.

and

$$W_{SO_2} = SO_{20} \frac{\%R}{(100 - \%R)} \quad (\text{Eq. G-7})$$

(Eq. G-7)

where:

W<sub>SO<sub>2</sub></sub>=Weight of sulfur dioxide removed, lb/day.

SO<sub>20</sub>=SO<sub>2</sub> mass emissions monitored at the outlet, lb/day, as calculated using the equations and procedures in section 2 of appendix F of this part.

%R=Overall percentage SO<sub>2</sub> emissions removal efficiency, calculated using Equations 1 through 7 in §75.15 using daily instead of annual average emission rates.

3.2 When a sorbent material other than limestone is used, modify the equations, methods, and procedures in Section 3.1 of this appendix as follows to estimate daily CO<sub>2</sub> mass emissions from sorbent (in tons).

3.2.1 Determine a site-specific value for F<sub>u</sub>, defined as the ratio of the number of moles of CO<sub>2</sub> released upon capture of one mole of SO<sub>2</sub>, using methods and procedures satisfactory to the Administrator. Use this value of F<sub>u</sub> (instead of 1.0) in either Equation G-5 or Equation G-6.

3.2.2 When using Equation G-5, replace MW<sub>CaCO<sub>3</sub></sub>, the molecular weight of calcium carbonate, with the molecular weight of the sorbent material that participates in the reaction to capture SO<sub>2</sub> and that releases CO<sub>2</sub>, and replace W<sub>CaCO<sub>3</sub></sub>, the amount of calcium carbonate used (in tons/day), with the amount of sorbent material used (in tons/day).

4. PROCEDURES FOR ESTIMATING TOTAL CO<sub>2</sub> EMISSIONS

When the affected unit has a wet flue gas desulfurization system, is a fluidized bed boiler, or uses other emission controls with sorbent injection, use the following equation to obtain total daily CO<sub>2</sub> mass emissions (in tons) as the sum of combustion-related emissions and sorbent-related emissions.

$$W_t = W_{CO_2} + SE_{CO_2}$$

(Eq. G-8)

where,

$W_t$  = Estimated total CO<sub>2</sub> mass emissions, tons/day.

$W_{CO_2}$  = CO<sub>2</sub> emitted from fuel combustion, tons/day.

$SE_{CO_2}$  = CO<sub>2</sub> emitted from sorbent, tons/day.

[58 FR 3701, Jan. 11, 1993, as amended at 60 FR 26556-26557, May 17, 1995; 61 FR 25585, May 22, 1996]

## APPENDIX H TO PART 75—REVISED TRACEABILITY PROTOCOL NO. 1

This appendix consists of section 3.0.4 of the Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. 3, U.S. Environmental Protection Agency (revised 6/9/87). The Quality Assurance Handbook may be obtained from the Methods Research and Development Division, MD 78-A, Atmospheric Research Exposure and Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

3.0.4. Procedure for NBS-Traceable Certification of Compressed Gas Working Standards Used for Calibration and Audit of Continuous Source Emission Monitors (Revised Traceability Protocol No. 1)

| Subsection | Contents  |
|------------|---|
| 3.0.4.0    | General Information   |
| 3.0.4.1    | <i>Procedure G1</i> : Assay and Certification of a Compressed Gas Standard Without Dilution |
| 3.0.4.2    | References  |

## 4.0 General Information

## 4.0.1 Purpose and Scope of the Procedure

Section 3.0.4 describes a procedure for assaying the concentration of gaseous pollutant concentration standards and certifying that the assay concentrations are traceable to an authoritative reference concentration standard. This procedure is recommended for certifying the local working concentration standards required by the pollutant monitoring regulations of 40 CFR Part 60<sup>1,2</sup> for the calibration and audit of continuous source emission monitors. The procedure covers

certification of compressed gas (cylinder) standards for CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, and SO<sub>2</sub> (Procedure G1).

## 4.0.2 Reference Standards

Part 60 of the monitoring regulations<sup>1,2</sup> requires that working standards used for calibration and audit of continuous source emission monitors be traceable to either a National Bureau of Standards (NBS) gaseous Standard Reference Material (SRM) or a NBS/EPA-approved Certified reference material (CRM)<sup>3</sup>. Accordingly, the reference standard used for assaying and certifying a working standard for these purposes must be an SRM, a CRM, or a suitable intermediate standard (see the next paragraph). SRM cylinder gas standards available from NBS are listed in Table 7.2 at the end of subsection 4.0. A current list of CRM cylinder gases and CRM vendors is available from the Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U.S. EPA, Research Triangle Park, NC 27711.

The EPA regulations define a "traceable" standard as one which "... has been compared and certified, either directly or via not more than one intermediate standard, to a primary standard such as a ... NBS [gaseous] SRM or ... CRM"<sup>4,5</sup>. Certification of a working standard directly to an SRM or CRM primary standard is, of course, preferred and recommended because of the lower error. However, an intermediate reference standard is permitted, if necessary. In particular, a *Gas Manufacturer's Intermediate Standard* (see subsection 4.0.2.1) that has been referenced directly to an SRM or a CRM according to Procedure G1 is an acceptable intermediate standard and could be used as the reference standard on that basis. However, purchasers of commercial gas standards referenced to an intermediate standard such as a GMIS should be aware that, according to the above definition, such a standard would have to be used directly for calibration or audit. Since a second intermediate standard is not permitted, such a standard could not be used as a reference standard to certify other standards.

4.0.2.1 *Gas Manufacturer's Intermediate Standard (GMIS)*. A GMIS is a compressed (cylinder) gas standard that has been assayed with direct reference to an SRM or CRM and certified according to Procedure G1, and also meets the following requirements:

1. A candidate GMIS must be assayed a minimum of three (3) times, uniformly spaced over a three (3) month period.
2. Each of the three (or more) assays must be within 1.0 percent of the mean of the three (or more) assays.
3. The difference between the last assay and the first assay must not exceed 1.5 percent of the mean of the three (or more) assays.

4. The GMIS must be recertified every three months, and the reassay must be within 1.5 percent of the previous certified assay. The recertified concentration of the GMIS is the mean of the previous certified concentration and the reassay concentration.

4.0.2.2 *Recertification of Reference Standards.* Recertification requirements for SRMs and CRMs are specified by NBS and NBS/EPA, respectively. See 4.0.2.1 for GMIS recertification requirements.

#### 4.0.3 Using the Procedure

The assay/certification procedure described here is carefully designed to minimize both systematic and random errors in the assay process. Therefore, the procedure should be carried out as closely as possible to the way it is described. Similarly, the assay apparatus has been specifically designed to minimize errors and should be configured as closely as possible to the design specified. Good laboratory practice should be observed in the selection of inert materials (e.g. Teflon, stainless steel, or glass, if possible) and clean, non-contaminating components for use in portions of the apparatus in contact with the candidate or reference gas concentrations.

#### 4.0.4 Certification Documentation

Each assay/certification must be documented in a written certification report signed by the analyst and containing at least the following information:

1. Identification number (cylinder number).
2. Certified concentration of the standard, in ppm or mole percent.
3. Balance gas in the standard mixture.
4. Cylinder pressure at certification.
5. Date of the assay/certification.
6. Certification expiration date (see 4.0.6.3).
7. Identification of the reference standard used: SRM number, cylinder number, and concentration for an SRM; cylinder number and concentration for a CRM or GMIS.
8. Statement that the assay/certification was performed according to this section 3.0.4.
9. Identification of the laboratory where the standard was certified and the analyst who performed the certification.
10. Identification of the gas analyzer used for the certification, including the make, model, serial number, the measurement principle, and the date of the last multipoint calibration.

11. All analyzer readings used during the assay/certification and the calculations used to obtain the reported certified value.

12. Chronological record of all certifications for the standard.

Certification concentrations should be reported to 3 significant digits. Certification documentation should be maintained for at least 3 years.

#### 4.0.5 Certification Label

A label or tag bearing the information described in items 1 through 9 of subsection 4.0.4 must be attached to each certified gas cylinder.

#### 4.0.6 Assay/Certification of Compressed Gas (Cylinder) Standards

4.0.6.1 *Aging of newly-prepared gas standards.* Freshly prepared gas standard concentrations and newly filled gas cylinders must be aged before being assayed and certified. SO<sub>2</sub> concentrations contained in steel cylinders must be aged at least 15 days; other standards must be aged at least 4 days.

4.0.6.2 *Stability test for reactive gas standards.* Reactive gas standards, including nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), and carbon monoxide (CO), that have not been previously certified must be tested for stability as follows: Reassay the concentration at least 7 days after the first assay and compare the two assays. If the second assay differs from the first assay by 1.5% or less, the cylinder may be considered stable, and the mean of the two assays should be reported as the certified concentration. Otherwise, age the cylinder for a week or more and repeat the test, using the second and third assays as if they were the first and second assays. Cylinders that are not stable may not be sold and/or used for calibration or audit purposes.

4.0.6.3 *Recertification of compressed gas standards.* Compressed gas standards must be recertified according to this section 3.0.4 within the time limits specified in Table 7.1<sup>3,6,7</sup>. The reassay concentration must be within 5% of the previous certified concentration. If not, the cylinder must be retested for stability (subsection 4.0.6.2). The certified concentration of a recertified standard should be reported as the mean of all assays, unless a clear trend or substantial change suggests that previous assays are no longer valid.

TABLE 7.1.—RECERTIFICATION LIMITS FOR COMPRESSED GAS STANDARDS

| Pollutant             | Balance gas <sup>1</sup>    | Concentration range | Maximum months until recertification for cylinder material |       |
|-----------------------|-----------------------------|---------------------|--|-------|
|                       |                             |                     | Passivated Aluminum  | Other |
| Carbon monoxide ..... | N <sub>2</sub> or air ..... | ≥ 8 ppm .....       | 36   | 6     |

TABLE 7.1.—RECERTIFICATION LIMITS FOR COMPRESSED GAS STANDARDS—Continued

| Pollutant  | Balance gas <sup>1</sup>    | Concentration range   | Maximum months until recertification for cylinder material |       |
|--|-----------------------------|---|--|-------|
|  |                             |   | Passivated Aluminum  | Other |
| Nitric oxide .....                                 | N <sub>2</sub> .....        | ≥ 5 ppm .....   | 24   | 6     |
| Sulfur dioxide .....                               | N <sub>2</sub> or air ..... | 50–499 ppm .....  | 24   | 6     |
| Sulfur dioxide .....                               | N <sub>2</sub> or air ..... | ≥ 500 ppm .....   | 36   | 6     |
| Oxides of nitrogen .....                           | Air .....                   | ≥ 100 ppm .....   | 24   | 6     |
| Nitrogen dioxide .....                             | Air .....                   | ≥ 1000 ppm .....  | 24   | 6     |
| Carbon dioxide .....                               | N <sub>2</sub> or air ..... | ≥ 300 ppm .....   | 36   | 18    |
| Carbon dioxide and oxygen, (i.e. blood gas). ..... | N <sub>2</sub> .....        | ≥ 5% CO <sub>2</sub> , ≥0% O <sub>2</sub> .....             | 36   | 6     |
| Oxygen .....                                       | N <sub>2</sub> .....        | ≥ 2 percent .....   | 36   | 18    |
| Carbon dioxide and nitrous oxide .....             | Air .....                   | ≥ 300 ppm CO <sub>2</sub> , ≥300 ppb N <sub>2</sub> O ..... | 36   | 6     |
| Others not specifically listed .....               | .....                       | .....   | 6  | 6     |
| Multicomponent mixtures .....                      | .....                       | .....   | See <sup>2</sup>   | 6     |
| Mixtures with lower concentrations. .....          | .....                       | .....   | See <sup>3</sup>   | 6     |

<sup>1</sup> When used as a balance gas, “air” is defined as a mixture of O<sub>2</sub> and N<sub>2</sub> where the minimum concentration of O<sub>2</sub> is 10% and the concentration of N<sub>2</sub> is greater than 60%.

<sup>2</sup> This protocol may be used to assay and certify individual components of multicomponent standards, provided that none of the components interferes with the analysis of other components and provided that individual components must not react with each other or with the balance gas. A multicomponent standard can be certified for a period of time equal to that of its most briefly certifiable component. For example, a standard containing 250 ppm sulfur dioxide and 100 ppm carbon monoxide in nitrogen can be certified for 24 months because the shortest certification period is 24 months.

<sup>3</sup> This protocol may be used for the certification of standards with concentrations that may be lower than those listed in Table 7.1. The initial certification period for such a lower concentration standard is 6 months. After this period, the standards may be recertified. If the recertification demonstrates that the standard is not unstable, the second certification period for this lower concentration standard is the same time period as indicated for the corresponding concentration standard listed in Table 7.1.

**4.0.6.4 Minimum cylinder pressure.** No compressed gas cylinder standard should be used when its gas pressure is below 700 kPa (100 psi), as indicated by the cylinder pressure gauge.

**4.0.6.5 Assay/certification of multi-component compressed gas standards.** Procedure G1 may be used to assay and certify individual components of multi-component gas standards, provided that none of the components other than the component being assayed cause a detectable response on the analyzer.

#### 4.0.7 Analyzer Calibration

**4.0.7.1 Basic analyzer calibration requirements.** The assay procedure described in this section 3.0.4 employs a direct ratio referencing technique that inherently corrects for minor analyzer calibration variations (drift) and DOES NOT depend on the absolute accuracy of the analyzer calibration. What is required of the analyzer is as follows: 1) it must have a *linear* response to the pollutant of interest (see subsection 4.0.7.5), 2) it must have good resolution and low noise, 3) its response calibration must be reasonably stable during the assay/certification process, and 4) all assay concentration measurements must fall within the calibrated response range of the analyzer.

**4.0.7.2 Analyzer multipoint calibration.** The gas analyzer used for the assay/certification must have had a multipoint calibration within 3 months of its use when used with this procedure. This calibration is *not* used

to quantitatively interpret analyzer readings during the assay/certification of the candidate gas because a more accurate, direct ratio comparison of the candidate concentration to the reference standard concentration is used. However, this multipoint calibration is necessary to establish the calibrated range of the analyzer and its response linearity.

The multipoint calibration should consist of analyzer responses to at least 5 concentrations, including zero, approximately evenly spaced over the concentration range. Analyzer response units may be volts, millivolts, percent of scale, or other measurable analyzer response units. The upper range limit of the calibrated range is determined by the highest calibration point used. If the analyzer has a choice of concentration ranges, the optimum range for the procedure should be selected and calibrated. Plot the calibration points and compute the linear regression slope and intercept. See subsection 4.0.7.5 for linearity requirements and the use of a mathematical transformation, if needed. The intercept should be less than 1 percent of the upper concentration range limit, and the correlation coefficient (r) should be at least 0.999.

**4.0.7.3 Zero and span check and adjustment.** On each day that the analyzer will be used for assay/certification, its response calibration must be checked with a zero and at least one span concentration near the upper concentration range limit. If necessary, the zero and span controls of the analyzer should be adjusted so that the analyzer's response

(i.e. calibration slope) is within about  $\pm 5$  percent of the response indicated by the most recent multipoint calibration. If a zero or span adjustment is made, allow the analyzer to stabilize for at least an hour or more before beginning the assay procedure, since some analyzers drift for a period of time following zero or span adjustment. If the analyzer is not in continuous operation, turn it on and allow it to stabilize for at least 12 hours before the zero and span check.

**4.0.7.4 Pollutant standard for multipoint calibration and zero and span adjustment.** The pollutant standard or standards used for multipoint calibration or zero and span checks or adjustments must be obtained from a compressed gas standard certified traceable to an NBS SRM or a NBS/EPA CRM according to Procedure G1 of this section 3.0.4. This standard need not be the same as the reference standard used in the assay/certification. The zero gas must meet the requirements in subsection 4.0.8.

**4.0.7.5 Linearity of analyzer response.** The direct ratio assay technique used in Procedure G1 requires that the analyzer have a linear response to concentration. Linearity is determined by comparing the quantitative difference between a smoothly-drawn calibration curve based on all calibration points and a straight line drawn between zero and an upper reference point (see Figure 1). This difference is measured in concentration units, parallel to the concentration axis, from a point on the calibration curve to the corresponding point for the same response on the straight line.

For the general linearity requirement, the straight line is drawn between zero and the highest calibration point (Figure 1a). Linearity is then acceptable when no point on the smooth calibration curve deviates from the straight line by more than 1.5 percent of the value of the highest calibration concentration. An alternative linearity requirement is defined on the basis of the actual reference and candidate concentrations to be used for the assay. In this case, the reference and candidate concentrations are plotted on the

calibration curve, and the straight line is drawn from zero to the reference concentration and extrapolated, if necessary, beyond the candidate concentration (Figure 1b). The deviation of the smooth calibration curve from the straight line at the candidate concentration point then must not exceed 0.8 percent of the value of the reference concentration. This latter specification may allow the use of an analyzer having greater nonlinearity when the reference and candidate concentrations are nearly the same.

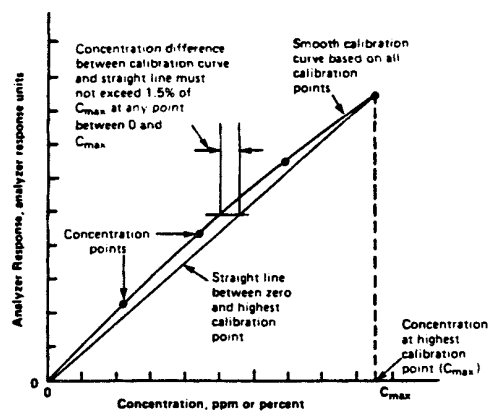
For analyzers having an inherently nonlinear response, the response can usually be linearized with a simple mathematical transformation of the response values, such as  $R' = \text{square root}(R)$  or  $R' = \log(R)$ , where  $R'$  is the transformed response value and  $R$  is the actual analyzer response value. Using the transformed response values, the multipoint calibration should meet one of the above linearity requirements as well as the requirements for intercept and correlation coefficient given in subsection 4.0.7.2.

#### 4.0.8 Zero Gas

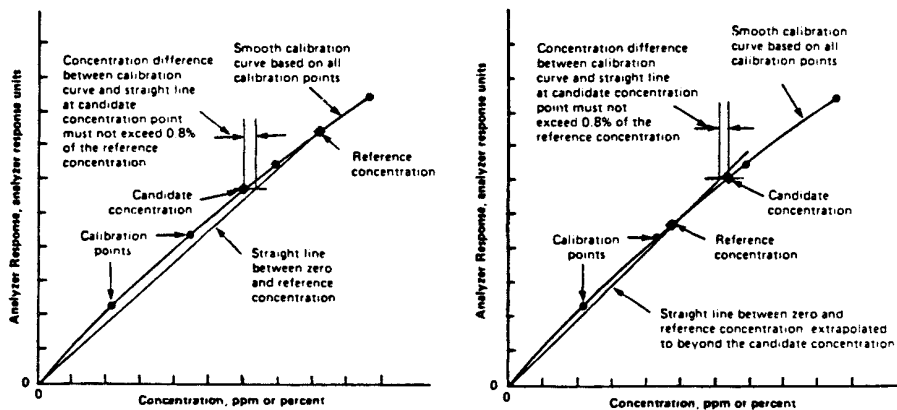
Zero gas used for dilution of any candidate or reference standard should be clean, dry, zero-grade air or nitrogen containing a concentration of the pollutant of interest equivalent to less than 0.5 percent of the analyzer's upper range limit concentration. The zero gas also should contain no contaminant that causes a detectable response on the analyzer or that suppresses or enhances the analyzer's response to the pollutant. The oxygen content of zero air should be the same as that of ambient air.

#### 4.0.9 Accuracy Assessment of Commercially Available Standards

Periodically, the USEPA will assess the accuracy of commercially available compressed gas standards that have been assayed and certified according to this section 3.0.4. Accuracy will be assessed by EPA audit analysis of representative actual commercial standards obtained via an anonymous agent. The accuracy audit results, identifying the actual gas manufacturers or vendors, will be published as public information.



a) General linearity requirement



b) Alternative linearity requirement

Figure 1. Illustration of linearity requirements.